

# A Universal Gaussian Basis Set for Atoms Cerium Through Lawrencium Generated with the Generator Coordinate Hartree–Fock Method

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*Received 30 October 1996; accepted 16 March 1997*

**ABSTRACT:** The generator coordinate Hartree–Fock method is applied to generate a universal Gaussian basis set for the heavy atoms from Ce ( $Z = 58$ ) through Lr ( $Z = 103$ ). The Hartree–Fock energies obtained with our universal Gaussian basis set are compared with the new numerical Hartree–Fock results of Koga et al., when available, and with geometrical Gaussian basis sets results available in the literature. The universal Gaussian basis set presented here is generated taking into account the shell constraint (the sharing of exponential functions between all s, p, d, and f atomic orbitals), and can be used as starting basis set in *ab initio* relativistic Hartree–Fock–Roothaan calculations. © 1997 John Wiley & Sons, Inc. *J Comput Chem* **18**: 1565–1569, 1997

**Keywords:** universal Gaussian basis set; generator coordinate Hartree–Fock method; heavy atoms

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Contract/grant sponsors: CNPq, FINEP

## Introduction

In 1986<sup>1</sup> the generator coordinate Hartree–Fock (GCHF) method was introduced as a new technique in the design of Gaussian- and Slater-type functions (GTF and STF, respectively). Since that time, the GCHF method has become one of the most powerful techniques in the generation of GTF and STF to be used in atomic and molecular calculations. One of its first applications was in the generation of universal Gaussian and Slater basis sets<sup>2–4</sup> and, afterwards, it was applied in the calculation of electronic properties of molecular systems.<sup>5</sup> Recently, the GCHF method has also been used successfully in the design of universal GTF exponents for relativistic calculations.<sup>6–9</sup>

As previously<sup>4</sup> we generated a universal Gaussian basis set for the atoms H through Xe and, recently, Koga et al.<sup>10</sup> reported accurate numerical Hartree–Fock (NHF) results for heavy atoms with atomic numbers  $Z \geq 55$ ; and in this work we employ the GCHF method with the aim to generate a universal Gaussian basis set for the heavy atoms Ce ( $Z = 58$ ) through Lr ( $Z = 103$ ). Here, we draw attention to the fact that we are presenting a flexible and accurate Gaussian basis set for atoms with  $58 \leq Z \leq 103$ . Before this, only Clementi<sup>11</sup> published accurate Gaussian basis sets involving a large number of heavy atoms (until Rn [ $Z = 86$ ]).

## Computational

As the details about the GCHF formalism can be found easily in the literature,<sup>1,4</sup> in this section we provide only a brief description of the GCHF method.

The GCHF method is a result of choosing the one-electron function as integral transforms:

$$\psi_i(1) = \int \phi_i(1, \alpha) f_i(\alpha) d\alpha, \quad i = 1, \dots, n \quad (1)$$

where  $\phi_i$  represents the generator functions (GTF in this work),  $f_i$  the weight functions, and  $\alpha$  the generator coordinate.

The  $\psi_i$  values are then used to build the Slater determinant and the mean value of the total en-

ergy,  $\langle E \rangle$ . With the variation of  $\langle E \rangle$  with respect to  $f_i$  one can obtain the Griffin–Wheeler–HF (GWHF) equations:

$$\int [F(\alpha, \beta) - \epsilon_i S(\alpha, \beta)] f_i(\beta) d\beta = 0, \\ i = 1, 2, \dots, n \quad (2)$$

where  $\epsilon_i$  are the HF eigenvalues, and  $F(\alpha, \beta)$  and  $S(\alpha, \beta)$  are, respectively, the Fock and overlap kernels (in Refs. 1 and 4, one can see explicitly the form of these kernels).

The GWHF equations [eq. (2)] are solved numerically by discretization through the integral discretization (ID) technique.<sup>12</sup> The ID technique is implemented through a relabelling of the generator coordinate space,  $\alpha$ , namely:

$$\Omega = \frac{\ln \alpha}{A}, \quad A \geq 1 \quad (3)$$

where  $A$  is a scaling parameter determined numerically. The new generator coordinate space,  $\Omega$ , is discretized for each s, p, d, and f symmetries in an equally spaced mesh  $\{\Omega_i\}$ . The set  $\{\Omega_i\}$  is then characterized by an initial point  $\Omega_{\min}$ , an increment,  $\Delta\Omega$ , and  $N$  (discretization point number), where  $N$  defines the GTF basis set size. The values of  $\Omega_{\min}$  (lowest value) and the highest value  $\Omega_{\max}$  ( $\Omega_{\max} = \Omega_{\min} + (N - 1)\Delta\Omega$ ) are chosen so as to adequately encompass the integration range for the s, p, d, and f weight functions for the atoms Ce ( $Z = 58$ ) through Lr ( $Z = 103$ ).

## Results and Discussion

By employing the GCHF method we generate a universal Gaussian basis set (UGBS) to describe the heavy atoms from Ce ( $Z = 58$ ) through Lr ( $Z = 103$ ). Our UGBS was generated from the following discretization parameters:

Symmetry	$\Omega_{\min}$	$\Delta\Omega$
s	−0.540	0.112
p	−0.428	0.112
d	−0.316	0.112
f	−0.204	0.112

With the discretization parameters  $\Omega_{\min}$  and  $\Delta\Omega$  just described for each of the s, p, d, and f symmetries, one can notice that we have a unique

set of GTF exponents where the GTF exponents for the p, d, and f symmetries are subsets of the GTF exponents of the s symmetry. Indeed, we have a unique set of GTF exponents where each starting exponent ( $\Omega_{\min}$ ) varies from one symmetry to another. One can see from the starting values of  $\Omega_{\min}$  for each of the s, p, d, and f symmetries that, if we take the  $\Omega_{\min}$  of the s symmetry ( $-0.540$ ) and add the value of  $\Delta\Omega$  ( $0.112$ ), we will obtain the  $\Omega_{\min}$  of the p symmetry ( $-0.428$ ), and so on. This sharing of exponential functions between all s, p, d, and f atomic orbitals is a generalization of the concept of a shell, which is utilized in programs such as GAMESS, GAUSSIAN, and HONDO to evaluate molecular integrals. This is why we have opted to generate our UGBS in such a way.

Table I shows the 33 exponents of our UGBS. In Table I, the 33 exponents represent a single set of GTF exponents that were used in our HF calculations for the atoms Ce through Lr.

**TABLE I.**  
**Exponents of UGBS.**

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0.03916390
0.07668877
0.15016809
0.29405160
0.57579706
1.12749685
2.20780763
4.32321786
8.46550778
16.57673158
32.45972208
63.56099525
124.46194419
243.71511946
477.23068961
934.48913473
1829.86962477
3583.15866841
7016.36109438
13739.08541667
26903.18607430
52680.46591150
103156.23885545
201995.35882388
395537.15256683
774520.95915274
1516627.98873367
2969784.65079438
5815282.94190191
11387194.58507861
22297831.73302219
43662492.66045550
85497697.18196450

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In Table II we show the total HF energies for the atoms Ce ( $Z = 58$ ) to Lr ( $Z = 103$ ) computed with our UGBS. The UGBS exponents used to obtain the HF energies shown in Table II were generated by employing the ID technique of the GCHF method [see eq. (3)]. They can be easily reproduced by using the discretization parameters,  $\Omega_{\min}$  and  $\Delta\Omega$  (displayed previously), and the UGBS size shown in Table II for each atom studied. The optimum scaling parameter,  $A$  [see eq. (3)] found for all calculations was 6.0. Here it is important to note that the GCHF method is one of the more flexible formalisms in the design of a universal basis set and, indeed, the ID technique of the GCHF method allows us to generate easily universal basis sets that are able to describe the HF total energy for a large number of atoms with good accuracy.<sup>4,13</sup> Moreover, another great advantage of the GCHF method is that it is an algorithm whereby basis function exponents are generated without being variationally optimized as commonly performed by other algorithms.

In Table II we compare the HF energies obtained from our UGBS with the recent NHF results obtained by Koga et al.,<sup>10</sup> when available, or with the NHF results of Fisher,<sup>14</sup> and with the geometrical Gaussian basis set (GGBS) results of Clementi et al.,<sup>11</sup>; however, Clementi and coworkers only generated GGBS data until the atom Rn ( $Z = 86$ ). In Table II, for each atom studied, we increased the number of exponents for each of the s, p, d, and f symmetries until a total HF energy value was attained with an accuracy comparable with that obtained from numerical calculation. In general, the UGBS size is always smaller than the GGBS of Clementi. When we compare the HF energies obtained with our UGBS and with the GGBS of Clementi et al. we can see that our results are a few millihartrees apart from the GGBS results, but we must remember that we have a universal basis set (a unique set of exponents that describe all atoms from Ce to Lr), whereas the GGBS is an adapted basis set (a different set of GTF exponents for each atom studied).

When we compare our UGBS energy results with the NHF results in Table II, we can see that from Ce ( $Z = 58$ ) to Rn ( $Z = 86$ ) our energy results are in very good agreement with the accurate NHF results of Koga et al. From Fr ( $Z = 87$ ) to Lr ( $Z = 103$ ), our UGBS energy results are, in general, only a few millihartrees apart from NHF results (except for Fr, Ac, and Lr, where the deviation of our UGBS results from the NHF results of Koga et al. is about  $10^{-2}$  hartrees).

TABLE II.  
Hartree – Fock Total Energies in Hartrees (Sign Reversed) of Atoms Ce (Z = 58) Through Lr (Z = 103).

Z	Atom	Configuration	State	UGBS size	UGBS <sup>a</sup>	GGBS size	GGBS <sup>b</sup>	Numerical <sup>c</sup>
58	Ce	[Xe]6s(2)4f(2)	<sup>3</sup> H	32s22p16d10f	8566.915116	—	—	8566.9196 <sup>d</sup>
59	Pr	[Xe]6s(2)4f(3)	<sup>4</sup> I	32s22p16d10f	8921.176919	32s25p17d16f	8921.180179	8921.181028
60	Nd	[Xe]6s(2)4f(4)	<sup>5</sup> I	31s22p16d11f	9283.879207	32s25p17d16f	9283.881730	9283.882944
61	Pm	[Xe]6s(2)4f(5)	<sup>6</sup> H	31s22p16d11f	9655.095389	32s25p17d16f	9655.097658	9655.098969
62	Sm	[Xe]6s(2)4f(6)	<sup>7</sup> F	31s22p16d11f	10034.94902	32s25p17d16f	10034.95126	10034.95255
63	Eu	[Xe]6s(2)4f(7)	<sup>8</sup> S	32s22p16d11f	10423.53966	32s25p17d16f	10423.54170	10423.54302
64	Gd	[Xe]6s(2)4f(8)	<sup>7</sup> F	31s22p16d11f	10820.61376	—	—	10820.617 <sup>d</sup>
65	Tb	[Xe]6s(2)4f(9)	<sup>6</sup> H	31s22p16d11f	11226.56456	33s26p18d16f	11226.56732	11226.56837
66	Dy	[Xe]6s(2)4f(10)	<sup>5</sup> I	31s22p16d11f	11641.44876	33s26p18d16f	11641.45090	11641.45260
67	Ho	[Xe]6s(2)4f(11)	<sup>4</sup> I	31s22p16d12f	12065.28623	32s24p17d14f	12065.28824	12065.28980
68	Er	[Xe]6s(2)4f(12)	<sup>3</sup> H	32s22p16d12f	12498.14947	32s24p17d14f	12498.15112	12498.15278
69	Tm	[Xe]6s(2)4f(13)	<sup>2</sup> F	32s22p17d12f	12940.17154	32s24p17d14f	12940.17256	12940.17440
70	Yb	[Xe]6s(2)4f(14)	<sup>1</sup> S	32s22p17d12f	13391.45325	32s24p17d14f	13391.45423	13391.45619
71	Lu	[Xe]6s(2)4f(14)5d(1)	<sup>2</sup> D	32s22p17d12f	13851.80163	31s24p20d14f	13851.80597	13851.80800
72	Hf	[Xe]6s(2)4f(14)5d(2)	<sup>3</sup> F	32s22p16d12f	14321.24418	31s24p20d14f	14321.24756	14321.24981
73	Ta	[Xe]6s(2)4f(14)5d(3)	<sup>4</sup> F	31s22p17d12f	14799.80815	31s24p20d14f	14799.81058	14799.81260
74	W	[Xe]6s(2)4f(14)5d(4)	<sup>5</sup> D	32s22p17d12f	15287.54302	31s24p20d14f	15287.54401	15287.54637
75	Re	[Xe]6s(2)4f(14)5d(5)	<sup>6</sup> S	31s22p17d12f	15784.52976	31s24p20d14f	15784.53083	15784.53319
76	Os	[Xe]6s(2)4f(14)5d(6)	<sup>5</sup> D	32s22p17d12f	16290.64466	32s24p20d15f	16290.64615	16290.64860
77	Ir	[Xe]6s(2)4f(14)5d(7)	<sup>4</sup> F	32s22p18d13f	16806.11067	32s24p20d15f	16806.11031	16806.11315
78	Pt	[Xe]6s(1)4f(14)5d(9)	<sup>3</sup> D	32s23p18d13f	17331.06713	32s24p20d15f	17331.06739	17331.06996
79	Au	[Xe]6s(1)4f(14)5d(10)	<sup>2</sup> S	32s23p17d13f	17865.39723	32s24p20d15f	17865.39726	17865.40008
80	Hg	[Xe]6s(2)4f(14)5d(10)	<sup>1</sup> S	32s23p17d13f	18408.98906	32s24p20d15f	18408.98771	18408.99149
81	Tl	[Xe]6s(2)4f(14)5d(10)6p(1)	<sup>2</sup> P	32s23p18d13f	18961.81863	31s25p18d13f	18961.82160	18961.82482
82	Pb	[Xe]6s(2)4f(14)5d(10)6p(2)	<sup>3</sup> P	32s23p17d13f	19524.00301	31s27p18d13f	19524.00458	19524.00804
83	Bi	[Xe]6s(2)4f(14)5d(10)6p(3)	<sup>4</sup> S	32s23p17d13f	20095.58177	32s27p17d13f	20095.58342	20095.58643
84	Po	[Xe]6s(2)4f(14)5d(10)6p(4)	<sup>3</sup> P	32s23p18d13f	20676.49741	31s27p17d13f	20676.49740	20676.50091
85	At	[Xe]6s(2)4f(14)5d(10)6p(5)	<sup>2</sup> P	32s23p18d13f	21266.87815	32s27p19d13f	21266.87870	21266.88171
86	Rn	[Xe]6s(2)4f(14)5d(10)6p(6)	<sup>1</sup> S	32s24p17d13f	21866.76857	32s27p19d13f	21866.76911	21866.77224
87	Fr	[Rn]7s(1)	<sup>2</sup> S	32s24p18d14f	22475.84828	—	—	22475.85871
88	Ra	[Rn]7s(2)	<sup>1</sup> S	33s23p18d14f	23094.29522	—	—	23094.30367
89	Ac	[Rn]7s(2)6d(1)	<sup>2</sup> D	32s24p18d14f	23722.17716	—	—	23722.19206
90	Th	[Rn]7s(2)6d(2)	<sup>3</sup> F	33s25p19d14f	24359.60899	—	—	24359.62244
94	Pu	[Rn]7s(2)5f(6)	<sup>7</sup> F	32s25p19d14f	27008.71075	—	—	27008.71944
95	Am	[Rn]7s(2)5f(7)	<sup>8</sup> S	32s25p19d14f	27695.87876	—	—	27695.88722
98	Cf	[Rn]7s(2)5f(10)	<sup>5</sup> I	32s25p19d14f	29817.41034	—	—	29817.41892
99	Es	[Rn]7s(2)5f(11)	<sup>4</sup> I	33s25p19d14f	30544.96419	—	—	30544.97219
100	Fm	[Rn]7s(2)5f(12)	<sup>3</sup> H	32s25p19d14f	31282.76778	—	—	31282.77760
101	Md	[Rn]7s(2)5f(13)	<sup>2</sup> F	33s25p19d14f	32030.92448	—	—	32030.93297
102	No	[Rn]7s(2)5f(14)	<sup>1</sup> S	32s25p19d14f	32789.50336	—	—	32789.51214
103	Lr	[Rn]7s(2)5f(14)6d(1)	<sup>2</sup> D	32s25p19d14f	33557.93826	—	—	33557.95041

<sup>a</sup>HF total energies obtained by using our universal Gaussian basis set.  
<sup>b</sup>HF total energies obtained by using geometrical Gaussian basis sets (Ref. 11).  
<sup>c</sup>Numerical HF total energies obtained from Ref. 10.  
<sup>d</sup>Numerical HF total energies obtained from Ref. 14.

The UGBS presented here for atoms Ce (Z = 58) through Lr (Z = 103), despite the importance of relativistic effects in these atoms, can be easily used as a starting basis set in relativistic calculations, as nonrelativistic wave functions are very often (as first performed by Matsuoka and Huzinaga<sup>14</sup>) carried over to relativistic calculations.<sup>6,8,9,15–19</sup>

Conclusions

The universal Gaussian basis set presented in this work showed flexibility and accuracy in describing the Hartree–Fock energies of the heavy atoms Ce (Z = 58) through Lr (Z = 103). It was designed with the shell constraint in mind (i.e., the

sharing of exponential functions between all atomic orbitals) and can be employed as a starting basis set in relativistic Hartree–Fock–Roothaan calculations involving the atoms from Cerium to Lawrencium. Once more, the generator coordinate Hartree–Fock method showed that it is a very powerful method in the design of basis sets for use in *ab initio* atomic and molecular calculations.

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